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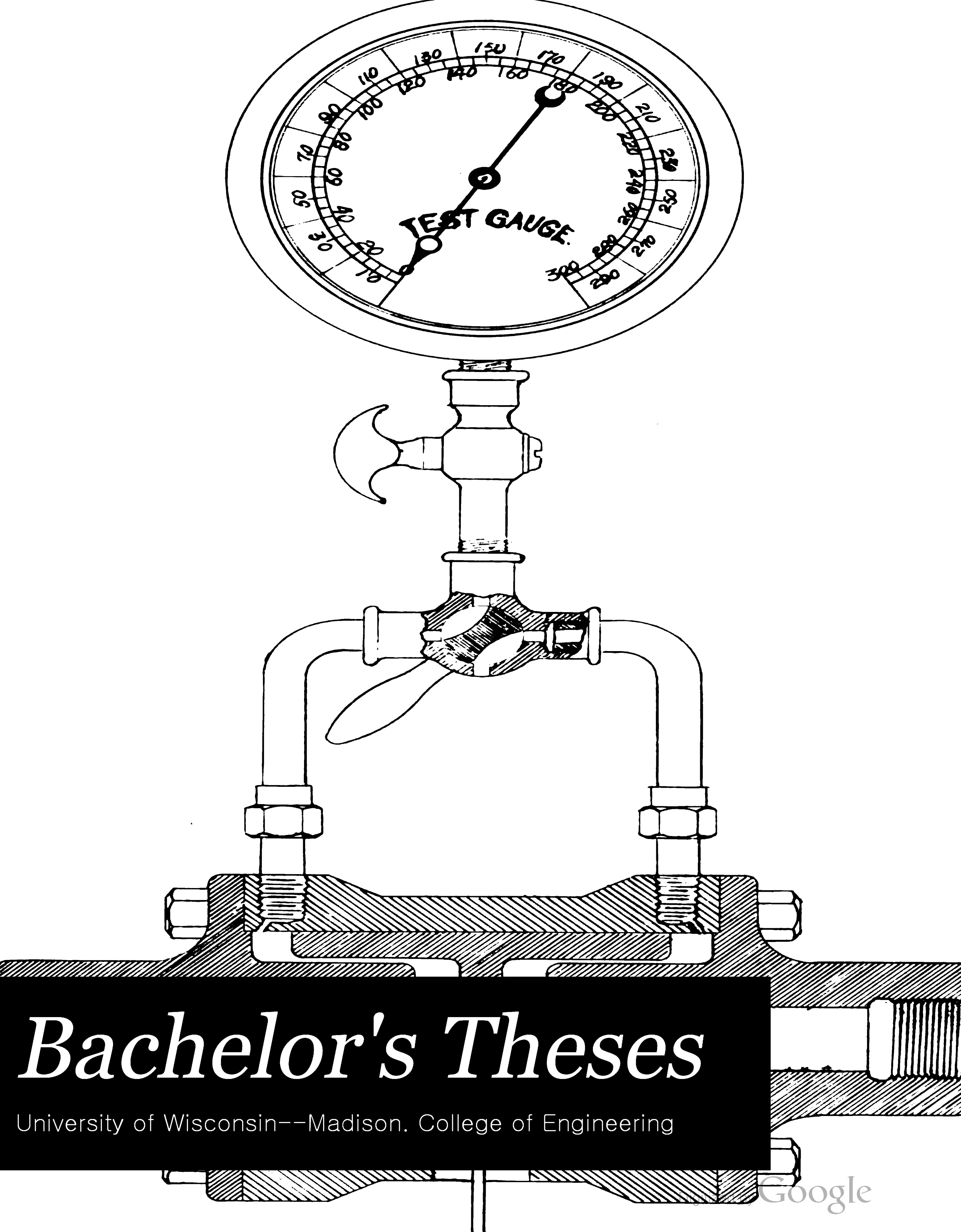

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THE SPECIFIC HEATS OF FLUIDS
AS FUNCTIONS OF TEMPERATURE AND PRESSURE

by

EARLE SMEAD BURNETT

A Thesis Submitted for the Degree of

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INTRODUCTION.

When the subject of this thesis was originally selected by the writer, the magnitude of its scope was not appreciated. A hasty examination into its literature failed to reveal the specific information desired, and a direct experimental determination was at once considered. Gradually as the literary search was extended without yielding that specific information, and as the detailed problems of the necessary experimental equipment appeared, he became conscious of the fact that any adequate treatment of the subject either literary or experimental demanded far more time than was at his disposal. Hence this thesis is presented as a preliminary report. The first part is in fact largely a sort of compilated resumé of the most relevant and important results that have come to his observation the past year in a search among the scientific records and literature available at this University; several days during two visits to Chicago were spent in research at the John Crerar Technical Library, where considerable valuable material was found. From the nature of this part there will unavoidably be some repitition; frequent comments and occasional abstracts have been made and reproductions of some of the most interesting graph-

ical illustrations have been prepared. Following this is an outline of the methods considered for experimental determination of the several relations which it is now desired to investigate ,and a description of some of the apparatus and arrangements that have been made for this purpose.

The literature on the thermal properties of fluids, which includes their specific heats, is voluminous; the number of investigators is proportionately as great and includes men from all parts of the scientific world. Especially is this true of thelast decade. To become familiar with the most important results in the original would require a reading knowledge of the English, German, French, Italian, Austrian, and Polish languages. Much of this has been translated into English, and most of it has been translated or abstracted into French or German. The attainments of the writer, however, have limited him almost entirely to English and German.

In nearly every case where quotations, direct or indirect, have been made, the credit and reference therefor have been indicated. As stated before this report is preliminary—the literature of the subject is far from exhausted, and some of the references found that appear most valu-

able have not yet been obtainable. But the attempt has been made to present enough to indicate the general status of the past and present investigations bearing on the specific heats of fluids, and their requirements of the immediate future.

The subject was first forcibly brought to the writer's attention in the perusal of an article* by Carl Linde on the efficiency of the regenerative process as applied to the production of liquid air by the method known as the self-intensification of cold. In his discussion of the thermal changes which the gas undergoes in passing through the apparatus, he showed by a simple application of known facts and thermodynamical principles, that only because of a change of its specific heat with temperature and pressure is it possible for any permanent or continuous production of cold to occur. By an application of the Joule-Thomson law for the cooling-effect experienced by gas in free expansion, extended to the limits under consideration, he deduced an expression for the specific heat of air as a function of pressure and temperature; from which he calculated several values showing that the effect of a decrease of temperature or an increase of pressure is to augment in a remarkable manner the specific heat of air at constant pressure. (See Plate VIII.

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*The Engineer, Vol. 82, 1896, p. 486, and 509.

The development of this relation as given by Linde will be presented later; suffice it here to say that the results derived were of so novel a nature and suggestive import as to arouse a desire to obtain evidence of their direct experimental confirmation. The fact that certain present and possible future commercial applications of fluids for the production of motive power or refrigeration, such as gas engines or turbines,and carbonic anhydride refrigerative machinery, depend, partially, for their success upon relations similar to those above indicated; or at least that an explanation of their apparently anomalous behavior under certain conditions, may be supported by these relations, furnished a further incentive to investigate them.

The feasibility of the application most interesting to the writer and one whose practicability is yet to be determined, depends directly upon the variation of specific heat with pressure, and in the study of the general subject so far, special effort has been made to learn—the influence of pressure on the specific heat (c_p) of a fluid, when the pressures involved are greater than its critical pressure; and the temperatures involved range from a minimum, where the fluid is in its dense and undercooled state, to a temper-

ature sufficiently great to maintain the fluid in a superheated gaseous state.

A cursory examination into the available literature of the subject, failed to reveal any direct experimental determination for air, but disclosed the fact that the thermal properties of CO_2 (Carbonic Anhydride) have probably been more widely and thoroughly investigated than those of any other fluid. Hence it was thought probable that some of the parties who deal commercially in CO_2 especially those designing and manufacturing CO_2 refrigerating machinery, might be posted as to the thermal relations desired. For this information a specific inquiry was sent to several dealers in materials of this nature. The replies were all of a negative value concerning the information desired, but revealed a surprising uncertainty as to the thermal relations in general, under certain conditions, frequently arising in practice, where the results commercially attained and the efficiency of the apparatus is far in excess of what physicists, until recently at least. have admitted possible. For CO_2 these conditions obtain when the temperature of condensing water is high. As the temperature of the liquid CO_2 rises, its heat of vaporization decreases, becoming zero

near 31°C. (88°F.). See Plate I. In the common refrigeration machines (compression machines, without expansion cylinders) using fluids like ammonia (NH_3) or sulphur-dioxide (SO_2), the cooling effect is produced by the (latent) heat of evaporation at low pressure. The heat here absorbed is given to the condensing water under a higher pressure and at a higher temperature as the heat of condensation and the superheat of compression. If, as with CO_2, the latter becomes zero, there can only be given to the condensing water the superheat of compression; but since the total heat absorbed by the condensing water, less the heat produced by the compression of the fluid, is a measure of the possible cooling effect or refrigeration that can be produced, it would appear that this also should approach zero as the temperature of the condensing water increases. As a matter of fact, the capacity of the CO_2 machines is considerably altered, but they are fully as efficient, commercially at least, (and per claims of their respective manufacturers), as are the NH_3 machines operating with the same temperature of condensing water. This is one of the anomalies previously referred to, and was the occasion of an oral comment to the writer by one of the parties addressed,

expressing a disbelief in the correctness of the values of the several thermal properties of CO_2 as given by various authorities and printed in their catalog. But so long as the machine is as efficient in warm climates as any other machine, and nearly as efficient as in colder climates unfer more favorable conditions, American makers, at least, are apparently not troubling themselves severely as to the causes. Methods of design appear to be based very largely upon practical results and observations rather than in combination with an intimate knowledge of the specific thermal properties involved in the use of the fluid under changing conditions.

Considerable work of a practical experimental nature to determine the behavior of CO_2 refrigerating machines has been done by Lorenz, Linde, Schroeter, and others in Germany. Their results,and others to be presented, lead the writer to the belief that this anomaly may be partially explained by the variation both of the specific heats of CO_2 and of the cooling-effect due to the so called free or unresisted expansion that the fluid undergoes in passing the expansion valve.

"In order to obtain a full knowledge of the thermodynamic properties of a homogeneous gaseous substance it is indispensible to make upon it a two-fold experimental investigation; besides its thermometric and dynamic behavior, its calorimetric properties ought to be studied independently. - - - - In the latter respect use may be made of the general laws of thermodynamics, - - - - from which it follows that in order to disclose the whole of the calorimetric properties of a homogeneous fluid, it is sufficient to investigate experimentally the specific heat in its dependence upon temperature, under a single constant pressure (usually taken as atmospheric); together with its compressibility and thermal expansion. - - - From these relations the variations of the specific heats as well as their differences can be deduced from the fundamental equation of the substance, viz. ; v = F(pt)."

Failing this equation, these variations can be obtained by the "graphical calculus" if the data therefor are available for diagramatic representation.

" The specific heat of atmospheric air under constant pressure has been repeatedly measured. In the first rank

there stands the fundamental work of Regnault[*]; fourteen years later these experiments were repeated by E. Wiedemann[#], with the help of a simpler form of apparatus. Regnault's experiments cover a range of temperature from $+200^{\circ}$C. to -31°C. Air of ordinary density was tried as well as condensed air up to 12 atmospheres. Notwithstanding these relatively extended limits Regnault was not able to discover any marked variation of the quantity c_p. Hence there arose the very general belief that the specific heat of air is a constant, independent of temperature and pressure—an opinion that as will be seen further on, is far from correct. Wiedemann's experiments were intended to control Regnault's value of the specific heat. The results obtained by the two experimenters are only in approximate agreement. According to Regnault the most probable value of the specific heat between 0° and 100° is 0.2374. Wiedemann's result is 0.2389." (Recently A. Ludec thought to have discovered an error in Regnault's experiments which if taken into account gave his value as 0.239, in almost exact agreement with results found by Wiedemann.)[©]

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[*] Relation des expériences etc., tome II, pp. 41-110, and pp 206-224. (Paris, 1862.)

[#] "Spez. Wärme der Gase," Pogg. Ann, Vol.clvii (1876) pp.19-22.

[©] Comptes Rendus 126, 1898, pp. 1860-61. Sci. Abs. 1898, No. 1234.

Witkowski*, (from whom the preceding has been quoted), in preparing to investigate the variation of the specific heat of air with temperature and pressure, thought it worth while to re-determine once more the exact value of this important 'constant'; especially so" since the thermodynamic scale of temperature is now better understood and our knowledge of the variation of the specific heat of water with temperature is more exact and extended." His result is nearly identical with that of Regnault. The experiments were carried to a temperature of -170°C. under atmospheric pressure. He concludes,"we may assert with certainty that the specific heat of air under atmospheric pressure does not vary in a sensible manner down to a temperature of -100°; and are warranted in considering it as a constant,(0.2372), from -100°C. down to -170°".

Lussana, experimenting at higher temperatures found the influence of temperature to be just the contrary (to that found by Witkowski), at low temperatures; but on the other hand it has been shown that for some gases the specific heat at constant atmospheric pressure increases with in-

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*Phil. Mag. S.5, Vol. 42, 1896, pp. 1-37.

creasing temperature. For instance for CO_2 Regnault gives:

Temp. °C.	Sp. Heat.
-28 to +7	0.1843
+15 to +100	0.2025
+11 to +214	0.2170

Wiedemann's figures are;

at 100	0.2169
" 200	0.2387

Recent experiments by Holborn and Austin* undertaken to determine the specific heat of atmospheric air and other gases for temperatures up to 1000°C. show a slight increase in that value, their maximum results for air being 0.2430 as the mean value between 20° and 800°. Their results however are probably less free from error than those of other investigators at lower temperatures.

Witkowski's results from his investigation of the specific heat of air at very low temperatures and very high pressures, depend upon a previous work of his own on the thermal expansion and compressibility of air#.

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*Preuss. Akad. Wiss. Berlin, Sitzber. 5, pp. 175-178, '05 Sci. Abs. 8, 1905, No. 765.

#Phil. Mag. S. 5, Vol. 41, 1896, pp. 288-312. Beiblätter 20, 1896, p. 639.

By aid of the formula,-

$$c_p = c_1 - \frac{t}{Jm}\int_1^p \frac{d^2v}{dt^2},$$

in which c_1 is the constant value of the specific heat of air at constant atmospheric pressure (0.2372), t is the absolute (thermodynamic) temperature of the isothermal, m the mass of the gas and J the dynamical equivalent of the heat unit, the values of c_p were determined by mechanical integration of the dilatation curves, for pressures from 10 to 100 atmospheres, and for temperatures of 0°, -50°, -100° and by 5° intervals to -145°. These values of c_p are plotted in two ways on Plates II and III; first as specific heat against pressure, on isothermal lines; and second as specific heat against temperature on lines of equal pressure (isopiestics or isobars). An examination of these curves will disclose the following relations;

The specific heat of air increases with the pressure and by far the more rapidly the lower the temperature. It furthermore attains a maximum at one particular and definite pressure different for each temperature, and diminishes thereafter with increasing pressure. At increasing temperatures these variations tend almost entirely to disappear.

The second set of curves, Plate III, show or suggest a little more. It is to be regretted that the necessary data is lacking with which to extend the curves to still lower temperatures. They suggest however that for each pressure there is some definite temperature, higher for higher pressures, at which the value of c_p is a maximum; that for those pressures and temperatures on the saturation curve this maximum tends toward an infinite value, probably abruptly at points below the critical. What occurs on the liquid side of the saturation curve is not evident from the diagram, though a possible more or less approximate reflection of the portion already determined is suggested. There are some seeming irregularities in the isobars above 50 atmospheres; some of these are probably due to experimental errors, though not all.

The specific heat at constant volume, c_v, is calculated from the formula,

$$c_v = c_p - \frac{t}{Jm}(d^2p/dt^2)/(dp/dv),$$

and is given for densities of the gas from $1/v = 10$ to $1/v = 100$, (where $v = 1$ under standard conditions), and for a series of temperatures from 0° to -140°. These values plotted on isothermal lines against pressure are shown in Plate

IV, Fig. 1. They show the relation of c_v to pressure to be practically linear, and also that the increase of c_v due to pressure is very great at the lower temperatures. The relation is not strictly linear as shown, but the deviation is too slight to be evident in the figure.

The ratios of $c_p/c_v = k$ (See Fig.2), are small at high temperatures but increase with the density throughout. At a temperature in the vicinity of -120°, k atains a maximum and then rapidly decreases with falling temperature.

In the direction of high temperatures Stevens[*] has found k to be 1.34 at 1000°C. A similar investigation with improved apparatus (acoustic method) was undertaken more recently by Alfred Kälahne[#] who determined k at 900° C. to be 1.39. These results are far from concordant, but they are in the same direction, showing a decrease in value compared to the normal value of about 1.4 (1.4025, Lummer and Pringsheim).[@] This is in agreement with the trend observed in the diagram above, Fig. 2.

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[*] Ann. d. Phys. 7, p. 285, 1902. See also Quincke, Wied. Ann. 63, p.66, 1897.

[#] Schallgeschwindigkeit und Verhältnis der Spez. Wärme der Luft bei hoher Temperatur." (J.A. Barth, Leipsic, 1902)

[@] Smithsonian Contrib., Vol. 29, 1903, No. 1126.

Without any doubt whatever the most thorough, extended and painstaking investigations ever undertaken and successfully completed, to determine the properties of fluids are the classic experiments of Amagat with air, hydrogen, nitrogen, oxygen, ethylene, carbon-dioxide, and others, published at intervals during the last 15 or 20 years. His researches on the dilatation and compressibility of these fluids, extended through a pressure range whose upper limit was not less than 1000 atmospheres in most cases, and as great as 3000 atmostpheres in some cases; and through a temperature range from 0° to 258°C. Every precaution possible was taken to obtain accurate data, and the results obtained furnish material of exceeding value in the attempt to determine the exact fundamental relations between pressure, temperature and volume of fluids.

The properties of CO_2 have been most widely discussed, as that fluid is typical of a certain type (tri-atomic) of imperfect gases, and its critical conditions are most easily attainable and studied. From an analysis of his data on CO_2 in both tabular and graphical form, Amagat has arrived at the following expression for the characteristic equation of this fluid, viz.-

$$p + v\frac{v - T(a + m\,\overline{v-b} + c\,\overline{v-b}^{-1})}{kv^{r} - \alpha + n\sqrt{(v-\beta)^{2} + d^{2}}} = RT,$$ in which a, b, c, d, k, m, n, R, α, and β are constants, p, v, and T being the variables.

This exceedingly complicated formula with three variables and nine constants is a marked contrast to the simple equation for the ideal gas, viz.- $pv = RT$. The history of the construction of this formula which satisfactorily represents the results obtained with pressures varying from 1 to 1000 atmospheres, and temperatures ranging from zero to 258°, is given at some length in Comptes Rendus, 128, 1899, pp. 538-542.

As has been observed before, if the variation of specific heat with temperature is known for one constant pressure, this value together with the knowledge of the compressibility and expansibility of a fluid suffices to determine the value of the specific heats at any temperature or pressure.

Amagat* has plotted 44 isopiestics on a volume-temperature diagram from the results of his experiments on CO_2. From these curves he has obtained by graphical differentiation the values of dv/dt for 25 temperatures, and plotted them as ordinates with temperatures as abscissae. From these

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*Comptes Rendus 130, p.1443,1900. Sci.Abs.3,1900, 165

second derived curves he has similarly obtained the values of d^2v/dt^2 and has plotted them with the corresponding pressures as abscissae. Thence by simple quadrature he obtains the difference between the isopiestic specific heats, since $J(dc_p/dp)_t = -t(d^2v/dt^2)_p$; i.e., the rate of change of specific heat at constant pressure with pressure when the temperature is constant, is proportional, but opposite, to the rate of change with temperature of the temperature-coefficient of expansion when the pressure is constant. This relation is shown by the very interesting and instructive set of curves reproduced on Plate V, in which for CO_2 the values of d^2v/dt^2 are plotted as ordinates of isotherms, against pressures as abscissae.

These curves show that for a temperature above the critical point, c_p increases with the pressure, at first rapidly (especially at low temperatures), attaining a maximum value at a pressure given by $d^2v/dt^2 = 0$, which (pressure) continually increases with the temperature; and afterwards diminishes, at first rapidly and then at a decreasing rate as the pressures continue to increase. (Compare Witkowski's curves for air). Also that for a temperature below the critical c_p increases with pressure until a state of saturation

is reached, but then undergoes an abrupt change (the sign of which is not a'priori assignable, but a method calculation is given), and afterwards decreases indefinitely and less and less rapidly as the pressure continues to increase, so that its maximum value occurs when the vapor is saturated, and therefore at a pressure which increases with t as before. Further, that the maximum value of c_p is the greater the nearer the corresponding point is to the critical point, being infinite at that point; lastly that for a gaseous state the variations of c_p decrease indefinitely becoming extremely small, and also, from and after a certain pressure for each temperature they decrease indefinitely with increase of pressure.

Probably the most valuable direct researches on the specific heat at constant volume, c_v, are those made by Joly* in Dublin. He determined for air, hydrogen and CO_2 the values of c_v at temperatures between 0° and 100°, for a pressure interval of nearly 100 atmospheres. The results for CO_2 graphically represented in Plate VI show that the specific heat c_v increases with the density; that within the limits of the experiments this relation is nearly linear;

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*Phil. Trans., Vol. 182, 1891, Vol. 185, 1894.

that the departure from a linear relation increases positively with increasing density; and furthermore that c_v increases with decrease in temperature. The relation of the mean c_v from about 10° to 100° to densities up to 0.15 is given by the formula $c_v = 0.1650 - 0.2125\rho - 0.3400\rho^2$. At decreasing densities the specific heat appears to approach the constant value of 0.1650.

Lussana[*] made experiments on c_v similar to those of Joly but with very discordant results. Later, however, he advances the view based upon experimental evidence, that the specific heat of air at constant volume referred to unit mass depends, for low pressures, on the density. This is certainly the case for other gases as well; for CO_2 the coefficient of variation of c_v with pressure, as determined by Lussana, is fully confirmed by the researches of Amagat.

C. Dieterici[#] experimented with CO_2 and isopentane. The values of the amounts of heat required to raise the temperature of the fluid confined at constant volume through observed ranges were determined, from which the actual internal specific heat S_1 (to use his notation), of the saturated

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[*] N. Cimento, 4, 6, pp. 81-93, 1897. Sci. Abs. 1898, 129.

[#] Ann. d. Phys. 12, 1. Sci. Abs. 1904, No. 1692

liquid at temperature T was deduced; and from these, together with Young's and Amagat's data, have been calculated the values of internal specific heats, k and k', of the liquid and vapor when just saturated. His conclusion is that k varies only slightly with the temperature but considerably with the volume having a maximum value for the critical volume. The accuracy of his deductions have however been severly criticized by E. Mathias.*

After Joly had determined the values of c_v above described, Amagat, with the aid of the formula,-

$$\frac{c_p}{c_v} = \frac{c_v + AT(dp/dt)(dv/dt)}{c_v}, \text{ in which}$$

let $N = AT\frac{dp}{dt}.\frac{dv}{dt}$, undertook from his own previous investigations, to determine the value of the ratio $k = c_p/c_v$ for CO_2. These calculations, for constant volume and a density of 0.124, while the temperature increased from 20° to 100°, and the pressure increased correspondingly from 45.1 to 69.5 atmospheres, gave a decrease of k from 1.930 to 1.592. On the other hand at a constant temperature of 50° and at pressure increased from 50 to 100 atmospheres the value of k increased from 1.705 to 4.633. Its normal

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*Sci. Abs. 8, 1905, No. 568.

value is 1.3 (1.2995, Lummer and Pringsheim). So it is seen that in any case k increases conjointly with the pressure, while at constant pressure k decreases rather rapidly with increase in temperature. See Plate VII. If the value of N for a definite temperature (50°) and a still higher pressure(up to 900 atmospheres) be calculated, it becomes evident, since there are no sudden changes in c_v probable, we may arrive at the conclusion that k reaches a maximum between 100 and 125 atmospheres, and then decreases regularly. At temperatures lying closer to the critical point these variations would appear much sharper, but exact data thereon is lacking. At higher temperatures on the contrary these variations become less pronounced, and the maximum through which the value of k passes, tends to disappear. Amagat sought to fill out the experimental defficiencies by an investigation of the corresponding ratio for hydrogen and air, which more approach the perfect condition. The values of N are here considerable smaller than with CO_2 but they likewise exhibit a maximum.

Experiments made by Lussana* tend to confirm Amagat's

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* N. Cimento 7, pp. 61-62; 365-376, 1898, 81-93, 1897. Sci.Abs. II, 1899, NO. 43.

law according to which the specific heat at constant pressure referred to unit mass of CO_2 increases rapidly with the pressure, reaches a maximum at about 110 atmospheres, and then diminishes up to 150 atmospheres, the limit of pressure reached in his (Lussana's) observations. This maximum tends to disappear with increase of temperature. In experimenting with mixtures of air and CO_2 it is found that as the proportion of air is increased the maximum observed in the case of CO_2 for the value of c_p at about 110 atmospheres, tends to disappear and become non-existent, when the proportion of air is sufficiently great.

In the first set of a later series of experiments under radically different methods of determining c_p it is shown that the mean variation of c_p per atmosphere is about 0.00111. The second set of the series confirms the empirical formula, $c_p = 0.23702 + 0.0015504(p-1) - 0.0000019591(p-1)^2$. Comparing these results with those of Amagat and Witkowski it is legitimate in infer that the specific heat at constant pressure, referred to unit mass, increases with the pressure, attains a maximum, and then decreases; that for air (within limits) it is represented by the above formula, and that, moreover, it varies with the temperature.

Before leaving this phase of the subject mention may be made here of the researches and writings of Möllier, Lorenz, and Linde on the thermal properties of CO_2, and the performance of CO_2 refrigerating machines. In the "Zeitschrift für die gesamte Kälte-industrie", 1895, 1896, Mollier has published a series of discussions in which on the basis of the numerous researches of Amagat on the pressure, volume, temperature relations of CO_2 in all states, he derived and computed formulae and tables for all its important thermal properties both in the saturated condition and without. Lorenz in the same magazine has a series of papers on the properties of superheated vapor and undercooled liquids and the phenomena involved in their expansion through throttle-valves, with special reference to CO_2 in refrigerating machines. At the present writing these papers have not been available for study, but the brief abstracts discovered indicate that they contain valuable relevant material.

Enough has now been given to indicate the very general realization of the fact that neither of the specific heats of a fluid nor probably any other of its thermal properties is constant in value except under special limited conditions; they are all more or less functions of temperature and

pressure or of density. The results of the most important observations on these relations for air and CO_2 that have come to the writer's notice have been presented in brief; much more might be mentioned bearing on the variations of specific heats regarding these and other fluids, especially steam, (for which an increase of c_p with superheat has been proven);but for present purposes what has been said will suffice.

We will return now to the discussion by Carl Linde[*], "On the Variation of the Specific Heat of Gases." It will be quoted in full:

"The question as to whether or not the specific heat of gases especially air depends upon their thermal condition, and how, is variously answered by physicists. While, upon the basis of the experiments of Regnault, E. Wiedemann and others, the specific heat of air at constant pressure, c_p, is generally considered to have a value that is independent of temperature and pressure, yet, referring only to the best known of the recent experimental investigations, Lussana[#] has found an increase of specific heat with in-

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[*] Sitzber. d. math.-phys. Classe d. kön. Bayer. Akad. d. Wiss. zu München, 1897, Bd. 97, pp.485-489.

[#] N. Cimento. 1894, pp. 70-87, 130-142.

creasing pressure, Mallard and le Chatelier[*] believe to have firmly established such an increase with increasing temperatures. (Compare Holborn and Austin).

"Specific heat has also been made the subject of theoretical investigations. Indeed c_p must have a constant value for a perfect gas, and therefore for a gas in which the attractive forces between the smallest particles are no longer effective, so that change of energy consists only in that part of the kinetic energy corresponding to translatory motion of the molecules. All departures from these conditions must in general result in change of c_p, and, in conformity thereto, such departures bear a definite relation to this change. So, for instance, from the variation of the coefficients of expansion, Witkowski has calculated the variation in c_p and has found it to increase with increasing pressure and decreasing temperature. Now a phenomenon which especially clearly shows the effect and magnitude of the internal work of the molecular attractive forces, is the cooling that a gas undergoes when, without doing external work, it expands from a higher to a lower pressure. I have already intimated[#] that there is an es-

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[*] Comptes Rendus 104, pp. 1780-82, 1887.
[#] Wiedemann's Ann., 1896, p. 328.

pecially simple and distinct relation between the variation of this cooling-effect and that of c_p.

"Investigation of this cooling-effect was undertaken many years ago by Joule and Thomson[*], within certain limits, for air, hydrogen and CO_2. These experimenters reduced the results of their observations to the following approximate formula for small pressure differences;

$$\delta = T - \theta = a\frac{p - p_0}{T^2} \text{ or } dT = a\frac{dp}{T^2} \quad --- \quad (1)$$

in which δ is the cooling from the the absolute initial temperature T, to the resulting absolute temperature θ, during the expansion from the pressure p to the pressure p_0, and a is a constant (for air 20808 with p expressed in kg. per sq. meter). From this relation the conclusion may be drawn as follows;

"If the quantity of heat, H, be removed from a current of gas under constant pressure p, so that the temperature falls from T_1 to T_2; if the gas then undergoes a further cooling to T_3 through expansion to p_0 and finally receives again the same quantity of heat H at constant pressure p_0 without any other change of energy taking place, then according to these conditions, and the above relations,

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[*] Phil. Trans. Roy. Soc., 1862, p. 579.

the final resulting temperature T_4 must be the same as that which would have occurred if the gas had expanded directly from T_1 and p to p_0 without the intermediate exchange of the quantity of heat $\mp$H. We have therefore the relation;

$$H = c_p\ (T_1 - T_2) = c_{p_0}(T_4 - T_3)$$

where c_p and c_{p_0} are the mean values of the specific heats at the constant pressures p and p_0, between the corresponding temperature limits. If $T_2 - T_3$ is greater than $T_1 - T_4$ then it follows that c_p is greater than c_{p_0}. For differential values of H,

$$dH = c_p\ dT = c_{p_0}\,(dT + d\delta)$$

and since δ increases with decreasing temperature,

$$c_p = c_{p_0}(1 - \frac{d\delta}{dT}) \quad - - - - - - - -(2)$$

"If the absolute temperatures are plotted on a diagram as ordinates and the corresponding values of δ as abscissae for a constant and definite pressure difference, $(p_1 - p_0)$, and at any point on the resulting so-called cooling-effect curve, a tangent is drawn making the angle ϕ with the axis of ordinates then we have:-

$$c_p = c_{p_0}(1 + \tan\phi) \quad - - - - - - - \text{I.}$$

"This relation as derived is general and in all strictness applicable, since it is developed without any

other hypotheses than those contained in the principle of the conservation of energy. According to this relation, for a knowledge of the variation of specific heat with pressure and temperature, it is essential to know the course of the cooling-effect curve for a particular and definite pressure difference. Numerical values of c_p for a particular gas can be found if a (numerical) expression for the law of the variation of this cooling-effect with temperature is given. On the supposition that the above equation (1) represents such an expression, then the following results;

$$dT = a\frac{dp}{T^2} \quad - - - - - - - - - (1)$$

The integration leads to,

$$T^3 - \theta^3 = 3a(p_1 - p_2)$$

$$\theta = \sqrt[3]{T^3 - 3a(p_1 - p_2)}$$

whence $\delta = T - \theta = T - (T^3 - 3a\,\overline{p_1 - p_2})^{1/3}$

and $$\frac{d\delta}{dT} = 1 - \frac{T^2}{(T^3 - 3a\,\overline{p_1 - p_2})^{2/3}}$$

or $$\frac{d\delta}{dT} = 1 - (T/\theta)^2$$

but since $d\delta/dT$ is a cooling-effect it is negative and the last expression may be written

$$\frac{d\delta}{dT} = (T/\theta)^2 - 1 = \tan\phi.$$

From I, $c_p = c_{p_0}(1+\tan\phi) = c_{p_0}(T/\theta)^2 \quad - - - - - - \text{II}.$

"Now for indefinitely small pressures c_p approaches a constant value as is evident from Witkowski's investigations at very low temperatures and pressures. If for atmospheric air this value is taken as 0.237 and a = 20808, then the following values for 1000 c_p are obtained: (See Plate VIII.)

	+100°C.	0°C.	-50°C.	-100°C
10 atmospheres	.239	242	245	258
40 "	.245	251	278	369
70 "	.251	277	331	846

(These values though not in close agreement with Witkowski's results follow for a part of their course the same general form. (Compare Plate II.) It will be observed however that the curves exhibit no sign of maximum and retrograde values as do those of Witkowski. This is undoubtedly due to the fact that in equation (1) from which they are derived, the cooling-effect for a definite pressure difference is expressed as a funtion of the absolute temperature only, and as independent of the absolute pressure, or density. While this is a very close approximation to the truth as revealed by the investigations of Joule and Thomson, for a limited range, it is almost certain that beyond these limits the dependence of the cooling-effect

upon absolute pressure or density is considerable, and if correctly determined and expressed in equation (1) would so modify the derivations dependent upon it as to give results in closer accordance with Witkowski's. Indeed Natanson*, experimenting with CO_2 at ordinary temperatures has shown that up to 25 atmospheres this cooling-effect increases with the pressure according to linear relations. Kester, for CO_2, at 22° discovered the relation that $dT/dp = 1.181 - 0.0015p$. (Sci. Abs. 8, 1905, No. 763.))

Linde continues,- "It is obvious that the above formula (II) ceases to be applicable as soon as the saturation temperature is reached at which liquifaction commences. At the critical state c_p must be infinite because here infinitesimal changes of temperature produce finite changes of volume. If we seek for the temperature at which $\phi = 90^{\circ}$ and c_p is infinite (under a pressure of 39 atmospheres, the critical pressure of air), we find from the above equation (II) that $T_c = -136^{\circ}$, which is a value lying near the actual critical temperature of air (-141°). Herein is confirmation not only for the correctness of the above considerations, but also for the assumption that the constants given by Joule and Thomson are applicable within very wide

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* [illegible] 51 [illegible]

limits. That the value of *a* cannot be a constant prevails from theoretical considerations, and is in accord with measurements I have been able to make in many experiments on the outflow of air under pressures up to 250 atmospheres. (Further information regarding these experiments the writer has been unable to find.) While for all pressures down to the liquifaction temperature an increase of cooling-effect in proportion to the inverse square of the absolute temperature is shown, the proportionality of this effect to the pressure difference as observed by Joule and Thomson, ceases to hold for high pressures; beginning at about 50 atmospheres a noticeable increase of *a* with increase in pressure is apparent.

"The prosecution of exact experiments for the determination of the cooling-effect of free expansion within wider pressure (and temperature) limits would furnish contributions of decisive value to establish the variation of the specific heat of gases."

Linde's method of determining specific heats appears to be fundamental in principle and of universal applicability within its proper limits. It depends as stated upon an exact knowledge of the dependence of the *temperature change*

of free expansion upon absolute temperature and pressure, or density. It seems strange that the results given by Joule and Thomson should have stood alone for so long, and have in general, been so universally applied and extended, with so little question, or without confirmation by repeated experiments. But of late much interest has developed in this direction, and work is under way extending the limits of the previous investigations. But few reports as yet, have been published, or come to the writer's attention.

This theory of Linde and others as just outlined, and upon which the operation of the Linde and Hampson air liquifiers is generally considered to be based, has recently been very vigorously attacked by Prof. Raoul Pictet*, who asserts that the production of cold in these machines is almost entirely due to external work done as the gas expands, increasing its volume against external pressure. It has long been held by most authorities on thermodynamics, that, at least with gases far removed from the saturated state, there can be no cooling in (insulated) throttled expansion, or wire-drawing, i. e. in the so called free or unresisted expansion,

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*"Theorie der Apparate zur Herstellung flüssiger Luft mit Entspannung."--Zeitschrift für komprimierte und flüssige Gase, Vol. 7, p. 21, et seq. 1903.

because, being unresisted, no *external* work is done; and hence whatever cooling-effect may occur, can only result from *internal work* between the molecules as modified by the extent of the departure of the gases from an ideal state. This has been the ordinary experience in compressed air work. The cooling that occurs in throttling from ordinary pressures is so small as to entirely escape notice; and it can therefore not be used for refrigerating purposes. Only by allowing the air to expand behind the piston of a motor and do external work can appreciable cooling-effect be observed; under these conditions it is considerable.

Pictet shows that according to Joule and Thomson's law the fall of temperature from 0°C. for a drop in pressure from 250 atmospheres to 1 atmosphere is 68.7°, while that due to the external work of increase of volume, as he claims is 61.1°. The disagreement here is considerable, but still not excessive. Similar calculations for an equal pressure drop from -141°C., the critical temperature of air, give respectively, 294° and 29-1/2°. The former value appears to be extravagant indicating (in temperature values) an *absolute negative* temperature of -162°. Regarding the latter value, 29-1/2°, he says;

"This is easily explained since the gas continually reduces in volume as the temperature falls. (and hence the increase in volume for a given pressure change also reduces). This entirely natural result stands in severe and incompatible opposition to the theory of Lindè. - - - - How is it possible that so colossal a difference that stands so completely at variance to all experience has not raised doubt among the distinguished scholars who are accustomed to working and investigation in these fields!" After an extended discussion of what he considers to be the actual events occurring in the operation of Linde's liquifier, aided throughout by simple numerical examples he concludes as follows: "This study has allowed us to follow in all their individuality the phenomena which successively or simultaneously occur in a machine for the liquifaction of air according to the system of Linde. We have seen that only the external work of pushing away the atmospheric air which presses against the inner tubes is the real cause of the cooling obtained that leads to the liquifaction of a definite quantity of air. In no manner do these machines form a special category of apparatus which utilize physical phenomena that in earlier apparatus remained unemployed (ohne Anwendung).

They are however reduced reproductions of the apparatus of Siemens and especially of that of Solvay. Indeed if we dispense with the motor in the machine described in the patents of Solvay, which can have no function, and replace it simply by the expansion of the compressed air which freely increases its volume against the external pressure, we arrive at an identity. The conception of the internal work of the gas upon which the patent of Herr von Linde rests, is incorrect" In another place he states that Linde appears to have perceived his error.

In a later number of the same magazine Pictet publishes an article* in which he derives the important comclusion that the cooling obtaining from the free expansion of a fluid after the 'molecular tumult' has subsided arises only from the external work of that gaseous part of the fluid which though pre-cooled is not liquified. For he considers that in the neighborhood of the liquid and especially the critical states, the apparently homogeneous mass of fluid really consists of a mixture of "liquogenic" and "gasogenic" molecules, and that the particular phenomena that may be observed in these conditions depend upon the proportion and distri-

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*Beitrag zur Theorie der Kompression und Entspannung von Gasen, Feb. et seq., Vol. 7, 8, 1904.

bution of these two kinds of molecules as they happen to be present, and the immediate past history of the fluid.

This latter view receives direct and partial support by the suggestions put forth by Thomas Preston in an article* "On the Continuity of Isothermal Transformation from the Liquid to the Gaseous State," in which he offers a possible explanation of the fact that during isothermal evaporation the volume of a fluid increases at constant pressure until the transformation is complete. The shape of the isothermals above the critical point and certain thermodynamic equations that represent them indicate that below this point the curve should take a double bend, crossing in three points the straight line representing the the observed occurrences connecting the liquid and gaseous states. If the influence of gravity could be removed from a homogeneous liquid, and heat uniformly applied, it would begin to evaporate all through its volume at the same time; the mass would then cease to be homogeneous, consisting of a heterogeneous collection of minute vapor bubbles throughout the liquid. As the transformation continues the bubbles grow and eventually the mass becomes a collection of liquid drops suspended

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*Phil. Mag. S. 5, Vol. 42, 1896, pp. 231-240.

throughout the vapor. If the bubbles and drops are continually uniform, according to the laws of vapor pressure and surface tension the pressure and volume relations would follow the curved line, during the transformation, instead of the straight one. But the conditions throughout are unstable; an unequal distribution of the bubbles, or drops, or a variation in their size, together with the hydrostatic pressure due to gravity render equilibrium impossible; the change then from one state to the other instead of being simultaneous for all particles is, so to speak, consecutive, and each part of the change being like the preceding the pressure remains constant until the transformation is complete.

However as the temperature and pressure of evaporation is increased the differences in density of the vapor and liquid become less, the differential action of gravity is smaller, and the relations between vapor pressure and surface tension change, so that the combined effect is to render more nearly stable a possible condition like the one just outlined. As the critical conditions are approached the stability is increased and beyond that the conditions would be stable. But for some distance either side of the critical the conditions, though changing rapidly, are still of

such a nature that a mass of fluid(CO_2 for instance) might indicate one temperature and yet actually contain enough particles of fluid corresponding in condition to another temperature, sufficient to influence the apparent thermal properties or capacities of the whole mass, and make any determination of future behavior dependent upon the immediate past history of the fluid as a whole.

An inspection of the curves, Plate I, showing the heat of evaporation and the saturation volumes of CO_2 as functions of temperature will perhaps serve to illustrate this possibility, for it is seen that the curves approach horizontality in the vicinity of the critical temperature, indicating that there, to very small changes of temperature correspond relatively great changes of heats of evaporation and of volume.

This then is a part of what Pictet refers to when he says, "This theoretical consideration, completely verified by experiments is of the utmost importance in the construction and superintendence of the operation of apparatus for the production of liquid air by its expansion from a higher to atmospheric pressure." He concludes, " After the detailed analysis of the occurrences during the expansion of a com -

pressed gas, it is evident that at present it is impossible to grasp or define the problem so that it can be expressed by a numerical law. The greatest defficiency at present is in our lack of knowledge concerning the inner structure of the molecule, its internal energy and "potential building". "It is necessary:- To determine by direct experimental evidence this potential and its numerical value, on the one side as a function of the absolute pressure, and on the other side as a function of the absolute temperature at which the compression occurs: To verify, by sensitive calorimeters, the differences that exist between the energy represented by the area of the compression diagram of the gas, and the heat actually produced or made sensible by its compression. Furthermore there must be exactly determined for each gas; (1) The increase of the 'apparent' specific heat just above the critical point, as a function of the pressure. (2) The corresponding increase of density of the gas both in relation to temperature and pressure just above the critical point."

Pictet is a physicist, scholar, and engineer of renown who has been considered an authority in matters of this nature. Yet in setting forth these new views on these important relations, he places himself in many respects completely

at variance with some hitherto existing conceptions that have become almost axiomatic among scientists. In this respect however, he is not entirely alone; there are others who have been doing some original thinking. Engineer C. Heinel of the technical high school of Berlin, in a paper*presenting the various phases of thermodynamic engine design by a method exceedingly interesting and lucid takes exception to some of the accepted and fundamental ideas of thermodynamics, but does it in a manner so logical and comprehensive as to incite considerable thought concerning the basis of previous views. For example he attacks one of the principal and original recognized indications of a so-called absolute zero of temperature, to wit, the proportionality to the temperature of the volume of a 'perfect' gas maintained under constant pressure. His reasons for this are graphically shown in Plate IX. Each of the straight lines (Fig. c) which represents the relation between temperature and volume increments within the proportional limits, if extended, cuts the axis of ordinates in a different point; furthermore the slope of the lines, that is, the expansion coefficient, is different for each different state of matter. From which it follows theoretically, that it is in-

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*Zeit.f.k. und fl. Gase, Sept. et seq. 1904-5.

correct to take as the absolute zero of temperature that point at which the line of the so-called permanent gases cuts the axis, in preference to a point determined by the intersection of any other line. The figures on Plate IX are quite self-explanatory, and illustrate the author's new conception with considerable force.

These discussions by Pictet and Heinel are here mentioned as important in their expression of new though radical conceptions by eminent scientists of some of the thermodynamic phenomena relative to the subject at hand.

Along with the pursuance of literary research on the subject of specific heats, the writer has had continually in mind methods that may be used for the experimental determination of the specific relations desired, should this knowledge otherwise fail to be forthcoming. Mention of progress in this respect therefore will not be out of place here; though it must be remembered that sources of information are as yet by no means exhausted, and that possibly no experiments may be necessary.

Several methods have suggested themselves to the writer or come to his attention. The first and perhaps the simplest

is the one by comparison. Consider a counter-current apparatus through which a fluid can pass in one direction, and return in the other. If the fluid enters at one temperature T_1, and pressure p_1, and returns at another temperature T_3 and pressure p_2, then the two currents flowing in opposite directions, and continually toward points of increasing or decreasing temperature will exchange a certain amount of heat. If there are no external losses, the amount, H, that one current loses the other gains, and vice versa; and the following relation holds;-

$$H = Wc_{p_1}(T_1 - T_2) = Wc_{p_2}(T_4 - T_3)$$

where W is the quantity of fluid in circulation per unit time, T_1, T_3, are the entering temperatures and T_2, T_4, the leaving temperatures at the pressures p_1 and p_2 respectively; c_{p_1} and c_{p_2} are the corresponding specific heats at the constant pressures; and H is the quantity of heat transferred per unit time. Since W is constant,

$$c_{p_1}/c_{p_2} = \frac{T_4 - T_3}{T_1 - T_2}.$$

If the variation of c_p with temperature is known for any one constant pressure p_0, then from the above, the absolute value of c_p at any temperature and pressure can be determined by direct proportion. In any case however

the method gives the relative value of the mean specific heats between practically the same temperature limits under two different and known pressures, which is the information originally desired. The advantages of this method are the following;- no knowledge is required of the quantity of fluid in use, which is a very decided advantage; no quantity of heat has to be measured; it is entirely independent of any thermal capacity of the apparatus; the only observations are temperature and pressure; the necessary apparatus is comparatively simple and inexpensive. All of these features are extremely desirable.

On the other hand however, the requirements for accuracy are somewhat conflicting. Radiation loss must either be determined or eliminated. By proper insulation and the circulation of large quantities of fluid per unit time it is possible to reduce the error due to this loss to a point where its effect on temperature measurement is in the vicinity of one one-hundredth of a degree. With what facility this may be done however awaits trial. Accurate determinations of the relation sought,demand that the temperature intervals be sufficiently large to reduce the errors due to instruments and their observations to a minimum;

but to obtain the ratio of c_{p_1}/c_{p_2} at a definite temperature, a very short range of temperature must be used, which will introduce with undue influence the errors just mentioned. Here then are two conflicting conditions for accurate results. But as previously stated the method is comparatively simple, and for the rough relative values originally desired, would be quite satisfactory.

As the study of the subject was continued there developed the desire to obtain more nearly accurate and absolute values of these properties, and methods of so doing were considered. These include an extension of the porous plug or free expansion experiment, as a check on other methods, and of value in itself. The direct method finally preferred is a modification of the continuous electrical calorimetric scheme used with so much success by Callendar and Barnes* in their determination of the variation of the specific heat of water with temperature. These investigators used short temperature intervals (about 8°C.) as a basis for determining the specific heat at the

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*Phil. Trans. Roy. Soc., 1902, Vol. 199A.

mean temperature of the interval. The fuid was caused to flow at a known rate, through a specially insulated tube, through which passed a wire carrying a current of electricity for supplying the energy necessary to produce the required temperature change, and in a manner that rendered its precise measurement very simple. The temperature intervals were measured with extreme precision by means of a differential platinum-resistance thermometer. Their determinations on the specific heat of water are undoubtedly the most reliable to date. However, this method could give only the mean specific heat over short temperature intervals, which is at best only an approximation to the specific heat at a definite temperature, and is almost if not quite entirely inapplicable to a fluid whose specific heat is changing rapidly with temperature as when under critical conditions.

The plan here proposed to use consists in measuring electrically the total amounts of energy required to raise a known amount of fluid circulating under constant pressure from a constant initial temperature to each of several higher temperatures distributed along a convenient range. In this way, by plotting these various quantities of heat against their resulting temperature changes, using the ini-

tial temperatures as origin, a curve may be drawn with considerable accuracy the slope of which at any point in terms of dQ/dT is the specific heat of the fluid at the corresponding temperature. This curve once accurately determined for any given pressure over a convenient temperature range may serve as a basis for its extension in either direction without limit; for it is only necessary to select another temperature interval, one of whose limits lies within the portion of the curve already determined, to locate a point in its extension. Slight irregularities due to unavoidable errors of observation are easily detected and smoothed out; while gross errors or abrupt or rapid actual changes of the relations are forcibly brought to view. The complete curve for a given pressure being determined and carefully drawn in fine lines to a suitable scale, may be enlarged if desired, for purposes of graphical differentiation. In this way the value of $c_p = dQ/dT$ at any temperature can be obtained with a high degree of accuracy.

It is to be noted that in the operation of this method, the fluid is circulated at a constant pressure. No compression is required beyond that needed to overcome friction of flow. The readings necessary are the electrical measure-

ments of volts and amperes, temperatures and pressures. Means of maintaining constant initial temperatures and constant conditions throughout each experiment must be provided; these constant conditions once realized,a short series of readings will suffice. It is necessary however to obtain with accuracy the rate of flow of the fluid, and this is one feature of the problem that is receiving careful attention. Since the quantity in circulation must be large and the pressures are high ordinary laboratory methods will not avail. Several methods are possible; by direct weighing,; by calibrated metering, either Venturi or ordinary water meter; or by displacement of the compressor corrected for slip: each of which presents special difficulties, and none of which determine,directly, the mass of the fluid passing per unit time, for in any case it will be necessary to determine the fluid density at the meter. This also presents some difficulties, but methods of solution that promise satisfaction are being developed. Obviously this electrical method is rather more complicated than the counter-current comparative method; but the greater precision of the results that may be therewith obtained fully justifies its use.

The cooling-effect method suggested by Linde is quite as accurate in principle, and appears to simplify experimental difficulties immensely. It is necessary, only, to obtain readings of pressure and temperature; provided the rate of flow of the quantity in circulation (i.e. the mass per second, not feet or meters per second) is sufficient to make the radiation and conduction losses negligible, for the cooling-effect is independent of quantity. Lack of time has prevented the details from being worked out, but the general scheme would be to construct a rather long porous plug capable of absorbing considerable pressure, and observing the rate of fall both of pressure and of temperature along the plug. The fluid should enter at a constant temperature and pressure, variable at pleasure, and be circulated at a constant rate by a compressor until a steady state is attained. Edgar Buckingham* has suggested a modification of this method whereby the heat necessary to obtain isothermal expansion of a gas through the plug is supplied and measured electrically, thus eliminating (perhaps) errors of conduction, and others due to

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*Phil. Mag. S. 6, Vol. 8, 1905, pp. 518-521.

the progressive change of temperature along the plug. His method however demands an exact knowledge of the specific heat in its relation to temperature at the various pressures, as well as of the rate of flow of the fluid in order to determine the tendency to change of temperature that is overcome by the heat supplied. Wherein its advantages over the original method lie is not apparent. By the use of a long plug as outlined above and the rate of fall of temperature and pressure along it for various initial temperatures and pressures, and for various total pressure drops through the plug, the value of dT/dp as a function of both temperature and pressure may be determined by a graphical device similar to the one just described, and from them the values of c_p as according to Linde.

The fall of temperature along the plug can probably best be determined electrically, by the change in resistance of a wire passing through it, as evidenced by the fall of potential along the wire. Two methods of determining pressure suggest themselves; it is evident that the pressures to be measured are small differences between large pressures, an observation that can be determined accurately only with some form of differential manometer. For

small differences the mercury column answers admirably; but the difficulty of obtaining glass tubes strong enough to stand with safety these high pressures is apparent. A new form of water column having a thick plate glass sight is obtainable however, that is guaranteed to resist 200 atmospheres. Ordinary mercury tubes placed within this can probably be made to meet the requirements with safety and satisfaction. When the pressure drops become very large the mercury gauges become unwieldy, and almost inapplicable, but in this case, for the same relative accuracy it is not essential to obtain measurements with the same absolute accuracy, as for the smaller differences.

Amagat in his experiments carried up to several thousand atmospheres, used a form of free piston manometer for measuring absolute pressure; in principle it is simply the hydrostatic press reversed, the reduced pressure being read by a mercury column. In a description* of an instrument of this kind, and of tests made to determine its precision in comparison with other forms of metallic manometers, it is shown that the experimental determination

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*E. Wagner, "Metallic manometers as high pressure instruments of precision"--Ann. der Phys. 15, 5, 1904, pp. 906-953. Sci. Abs. 8, 1905, No. 499.

of the effective areas, (which in one particular instrument has a ratio of 60 to 1) rendered its absolute indications certainly correct to plus or minus 0.05%, with a sensibility of plus or minus 0.025 atmosphere. The tests were carried up to 300 atmospheres. For present purposes there has been designed after this principle, and is now being constructed, a special form of differential free piston manometer shown in Plate X. It consists of three concentric and connected steel pistons or plungers ground to exact dimensions, and operating within corresponding cylinders of steel also ground to size leaving the least possible adequate clearance which should be as little as 1/10,000 of an inch. The internal spaces connected to the gauge valve, and those at the outer ends of each small plunger are filled with castor oil, serving to transmit pressure, to prevent leakage of gas and to lubricate the pistons. If two different and large pressures are applied to the smaller plungers, the three together will move in the direction of the greater pressure until, within the space in connection with the gauge, a pressure is developed by compression of the oil, sufficient to balance the difference of pressure on the two plungers. The dimensions are such that the area of each

plunger is equal to 1/2 sq. inch, while that of the annular large piston between them is 5 sq. inches, giving a ratio of 1 to 10. If p_1 is the greater unit pressure on one plunger, p_2 the lesser unit pressure on the other, and p the gauge pressure, then $p_1 - p_2 = 10p$ is the dimensional relation of pressures. By removing the pressure on one of the plungers p_2 becomes zero and the instrument then serves for measurement of absolute pressure. In order to allow the instrument to adjust itself to give correct indications, friction of movement or of rest must be eliminated as far as possible. This is effected by giving the pistons a slight rotatory motion by a pin extending through a window in the side of the barrel as shown; the motion may be given only at times of reading the pressure, or it may be made continuous by a suitably arranged pendulum or clockwork. For the most precise work a determination of the effective areas of the plungers, and their sensibility must be made. The instrument is designed for 'working' pressures up to 250 atmospheres, but should stand double that pressure with good results.

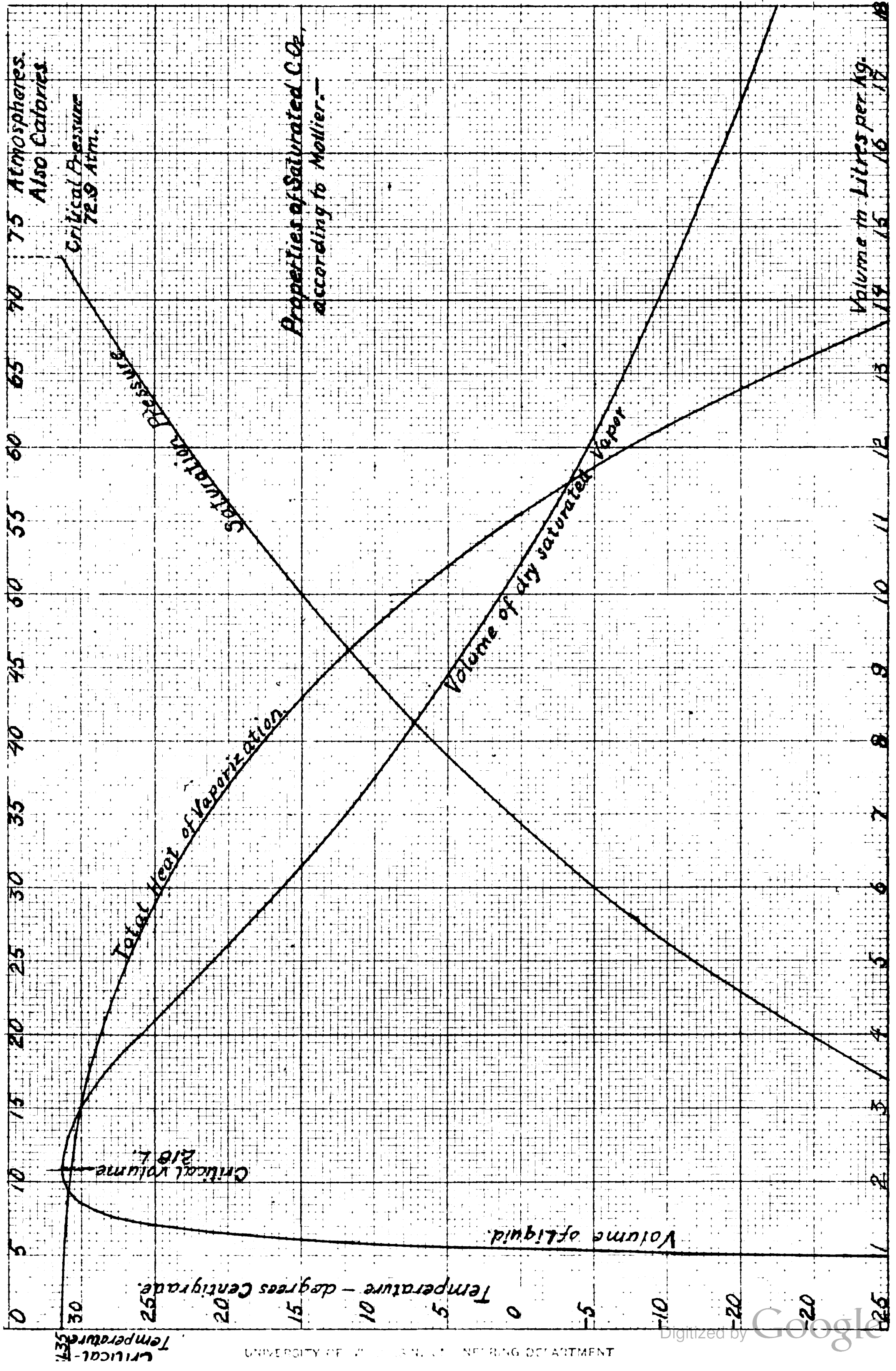
It is obvious that experiments at high pressures and very low temperatures require special apparatus and precau-

tions, and present special difficulties of preparation and operation. As apparatus of this kind was not available at this University a request was made by the writer several months since, to a Chicago firm dealing in CO_2 machinery, to consider a proposition whereby the desired determinations might be made with their apparatus at their factory where facilities for the handling of high pressures obtained. Correspondence and personal interviews with Mr. F. Wittenmeir, superintendent of Kroeschell Bros. Ice Machine Co., Chicago, have resulted in the offer on his part of the gratuitous use in Madison, for a reasonable length of time, of a suitable CO_2 compressor, any necessary fittings carried in stock, and a sufficient supply of CO_2 fluid, as commercially pure as can reasonably be obtained. These arrangements are very satisfactory indeed, and thanks are due Mr. Wittenmeir for the interest thus shown and the favors offered.

It is intended to continue for a time a research in the literature of the subject, in the hopes of finding some record of direct determinations that may already have been made. Failing this, the experimental work will be pushed as rapidly as conditions will permit with the appa--

ratus at disposal and that may be obtained or constructed as required. Several other related problems will be studied at the same time or later; for instance, the phenomena involved in the flow of highly compressed air or CO_2 through nozzles as in a turbine. Some phases of the work make it very desirable to extend the investigations to the field of liquid air if the apparatus therefor may be available. However, the details of both the investigation and apparatus are as yet to be developed, and as they are somewhat mutually interdependent upon progressive results, complete definiteness of plans cannot now be stated. It is expected to devote considerable time to the work the present summer and to continue it as a major study throughout the next collegiate year. The writer is enabled to continue largely through the assistance afforded him by a Scholarship in Mechanical Engineering, recently conferred by the faculty of the College of Engineering, and he hereby takes this opportunity to express his grateful appreciation of the substantial honor thus received.

PLATE I.


Properties of Saturated C O2, according to Mollier.—
Atmospheres.
Also Calories.
Critical Pressure 72.9 Atm.
Saturation Pressure
Total Heat of Vaporization
Volume of dry saturated Vapor
Volume in Litres per Kg.
Critical volume 2.18 L.
Volume of Liquid
Temperature — degrees Centigrade.
Critical Temperature
31.35
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
1
2
3
4
5
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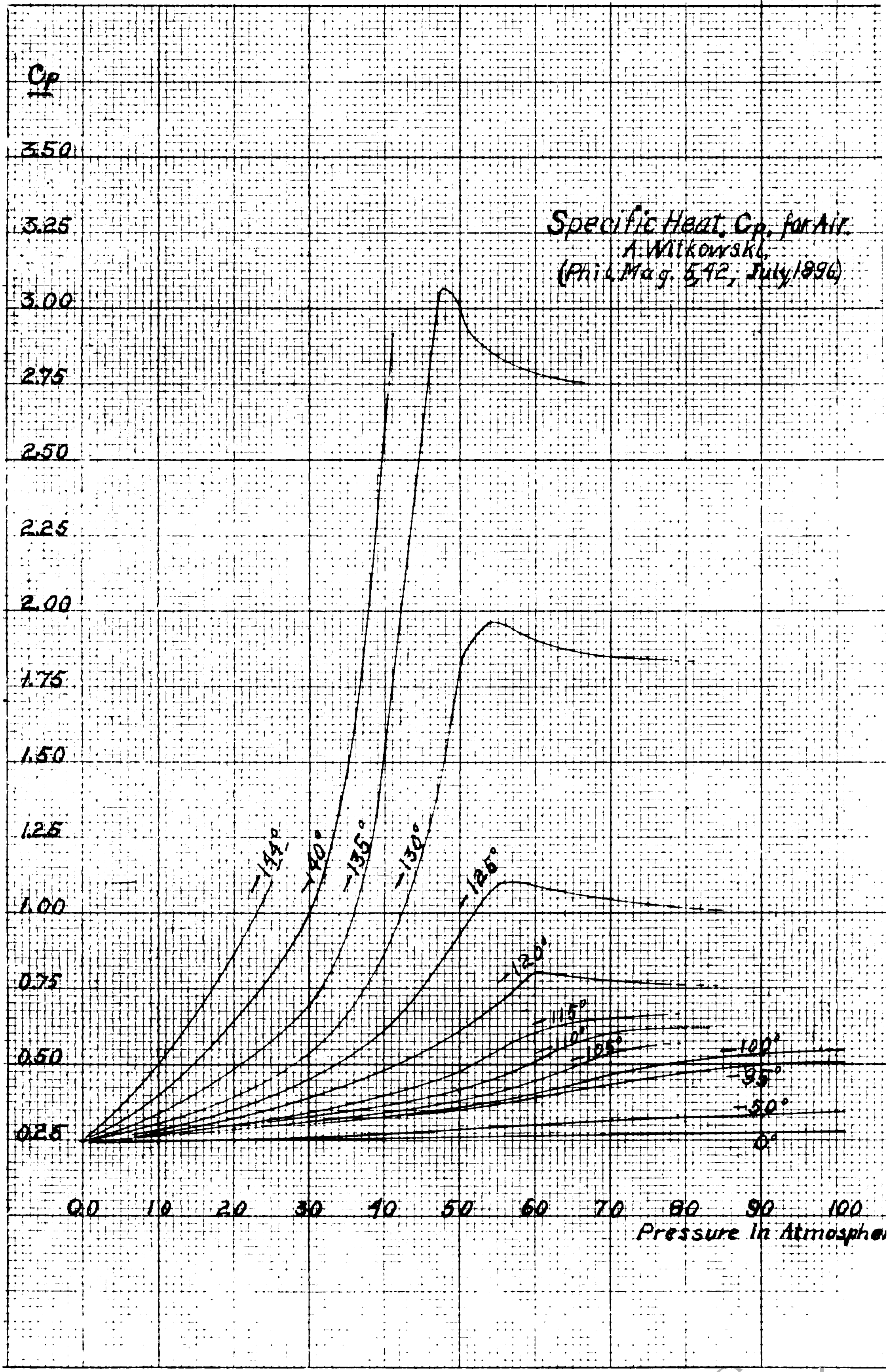
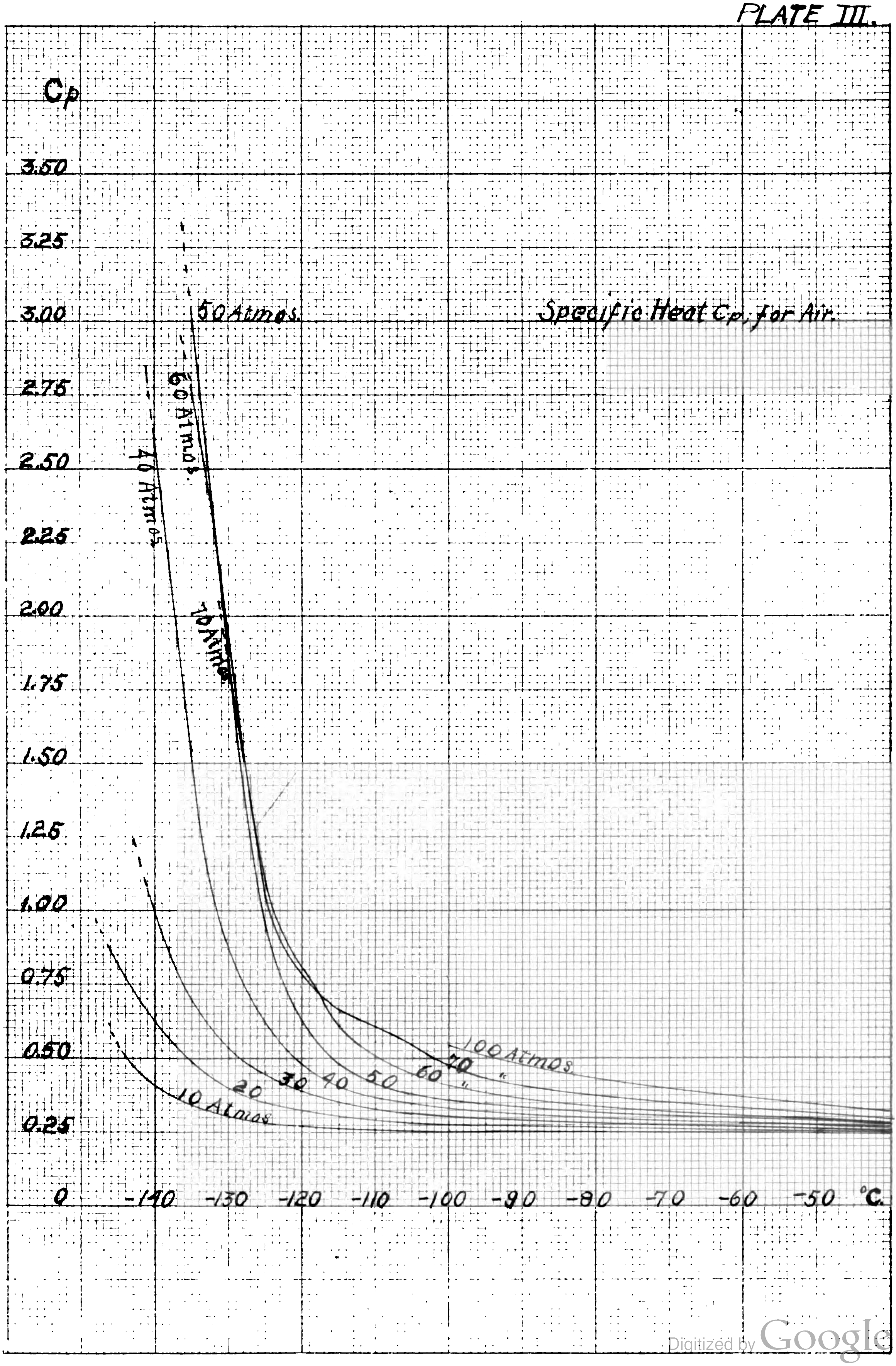
-20
-20
-25

PLATE.



Specific Heat, Cp, for Air.
A. Witkowski,
(Phil. Mag. 5,42, July 1896)

PLATE III.


Specific Heat Cp, for Air.

UNIVERSITY OF WISCONSIN, ENGINEERING DEPARTMENT

PLATE IV.

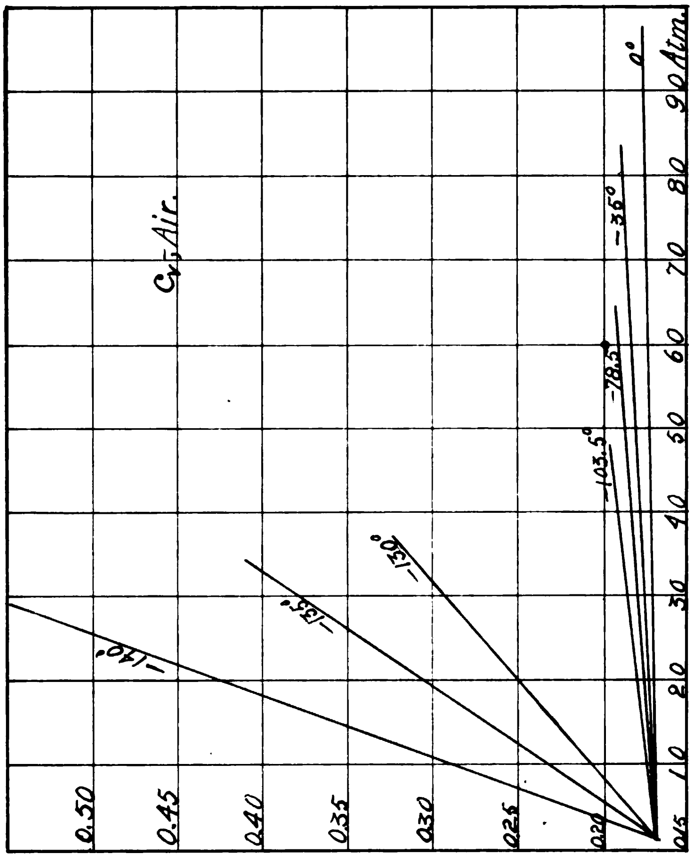


Fig. 1.

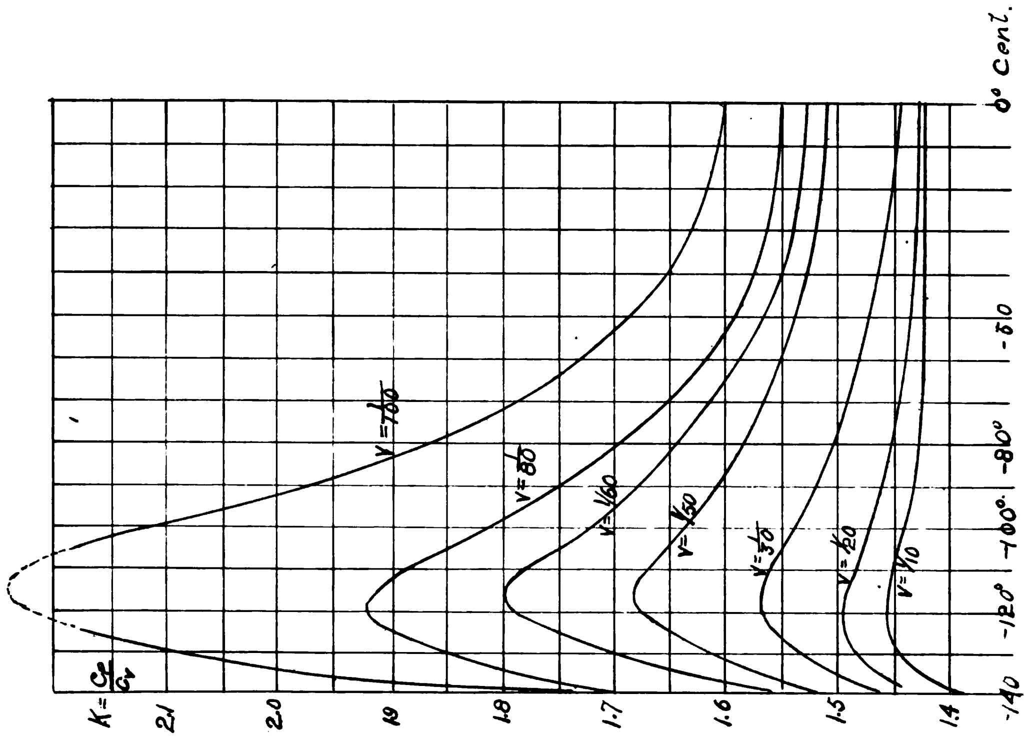
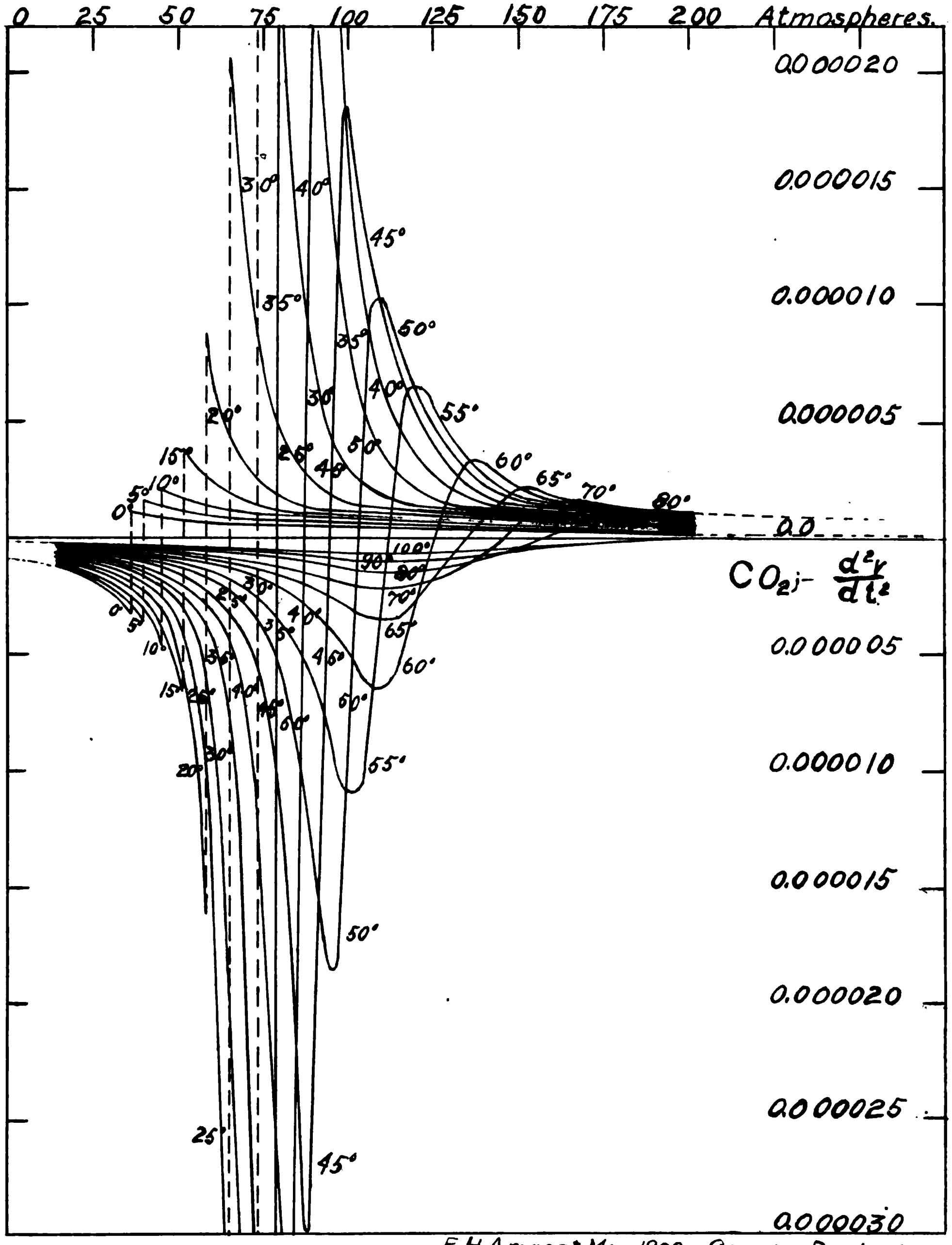


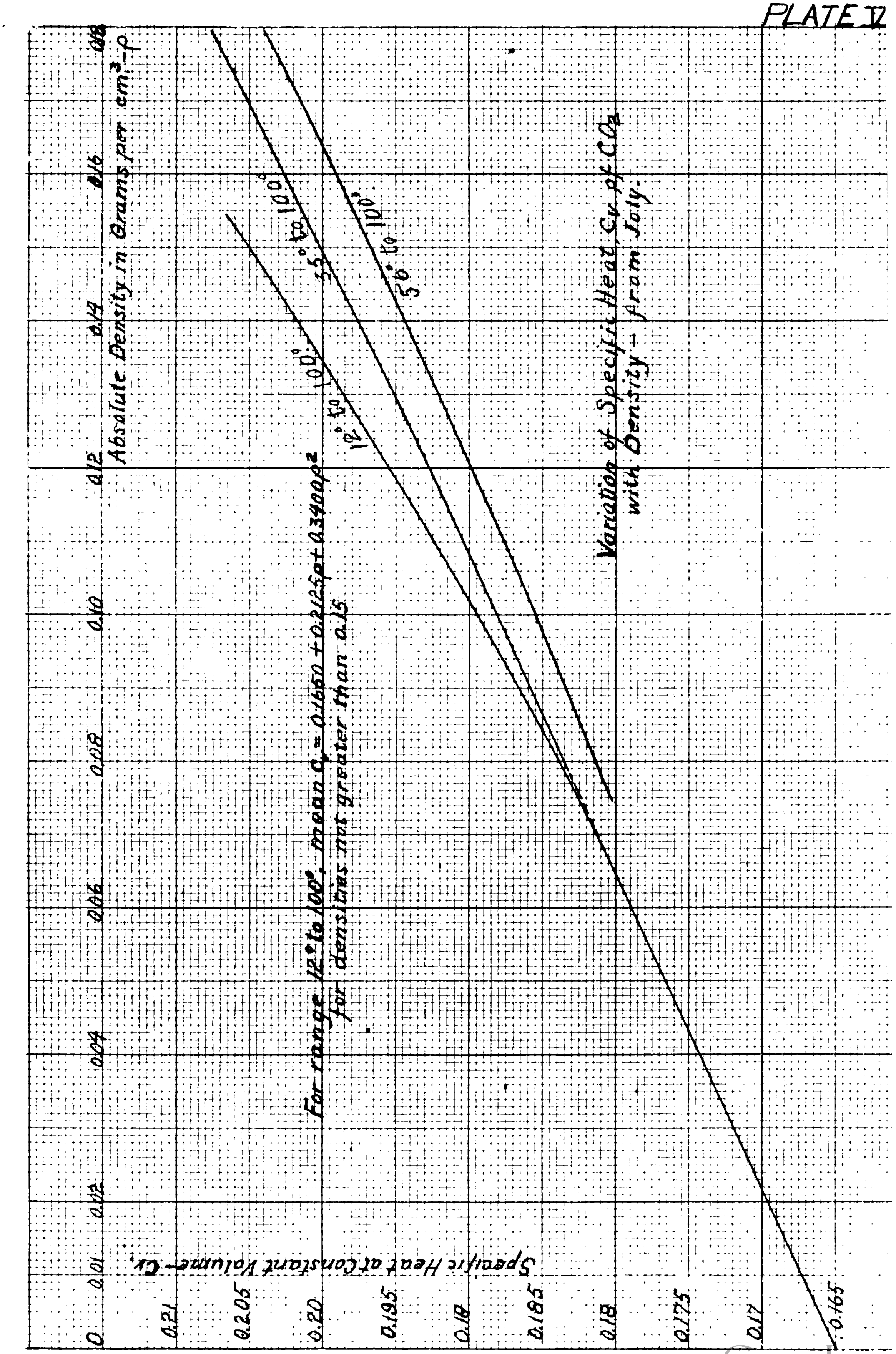
Fig. 2.

PLATE V.



E.H.Amagat, May 1900 —Comptes Rendus 130, p.1455.

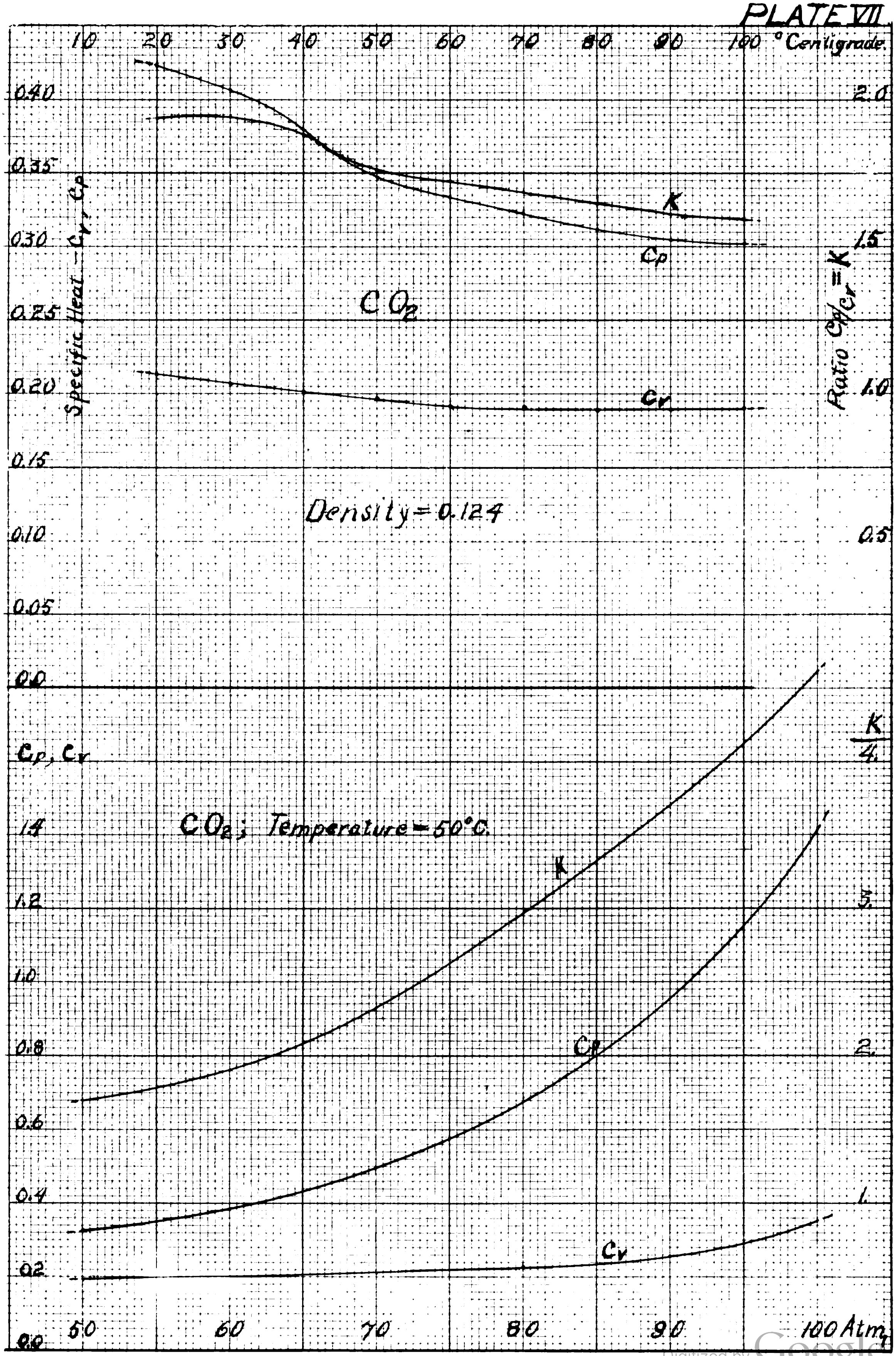
PLATE V



Variation of Specific Heat, Cv, of CO_2 with Density - from Joly.

For range 12° to 100°, mean $C_v = 0.1650 + 0.2125\rho + 0.3400\rho^2$ for densities not greater than 0.15

PLATE VII.


10
20
30
40
50
60
70
80
90
100 °Centigrade.
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.0
2.0
1.5
1.0
0.5
Specific Heat – C_v, C_p
Ratio $C_p/C_v = K$
K
C_p
C_v
CO_2
Density = 0.124
C_p, C_v
$\frac{K}{4}$
CO_2; Temperature = 50°C.
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
3.
2.
1.
K
C_p
C_v
50
60
70
80
90
100 Atm.

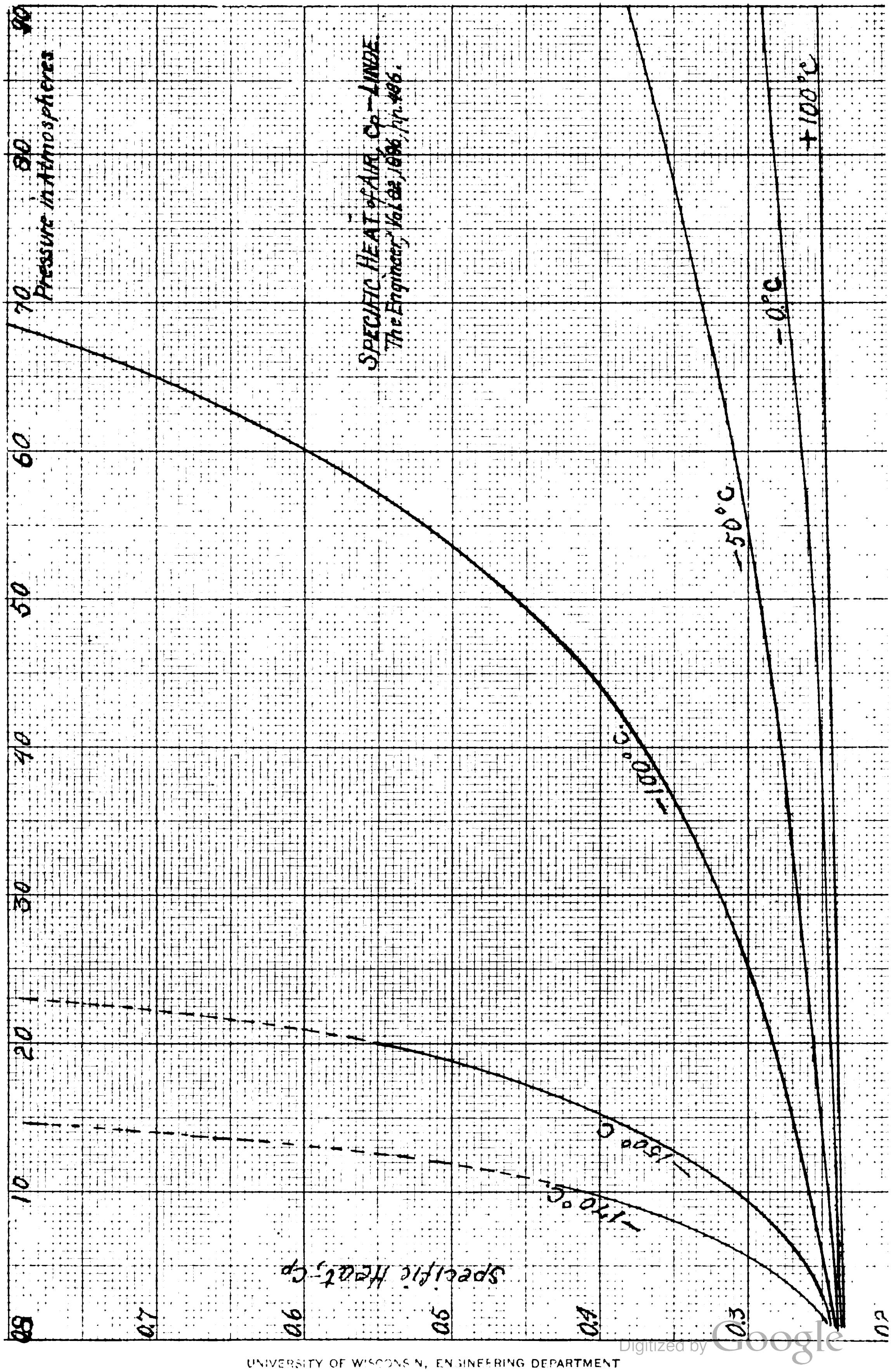


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PLATE IX.

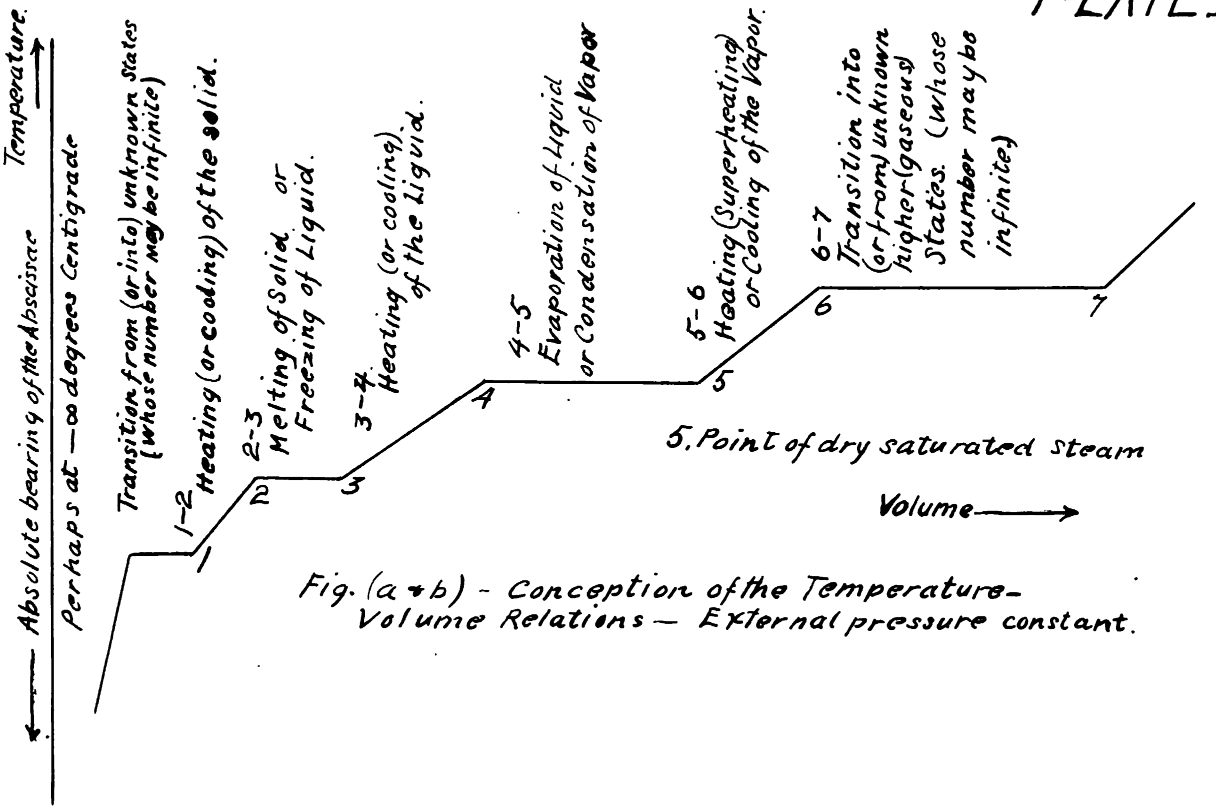
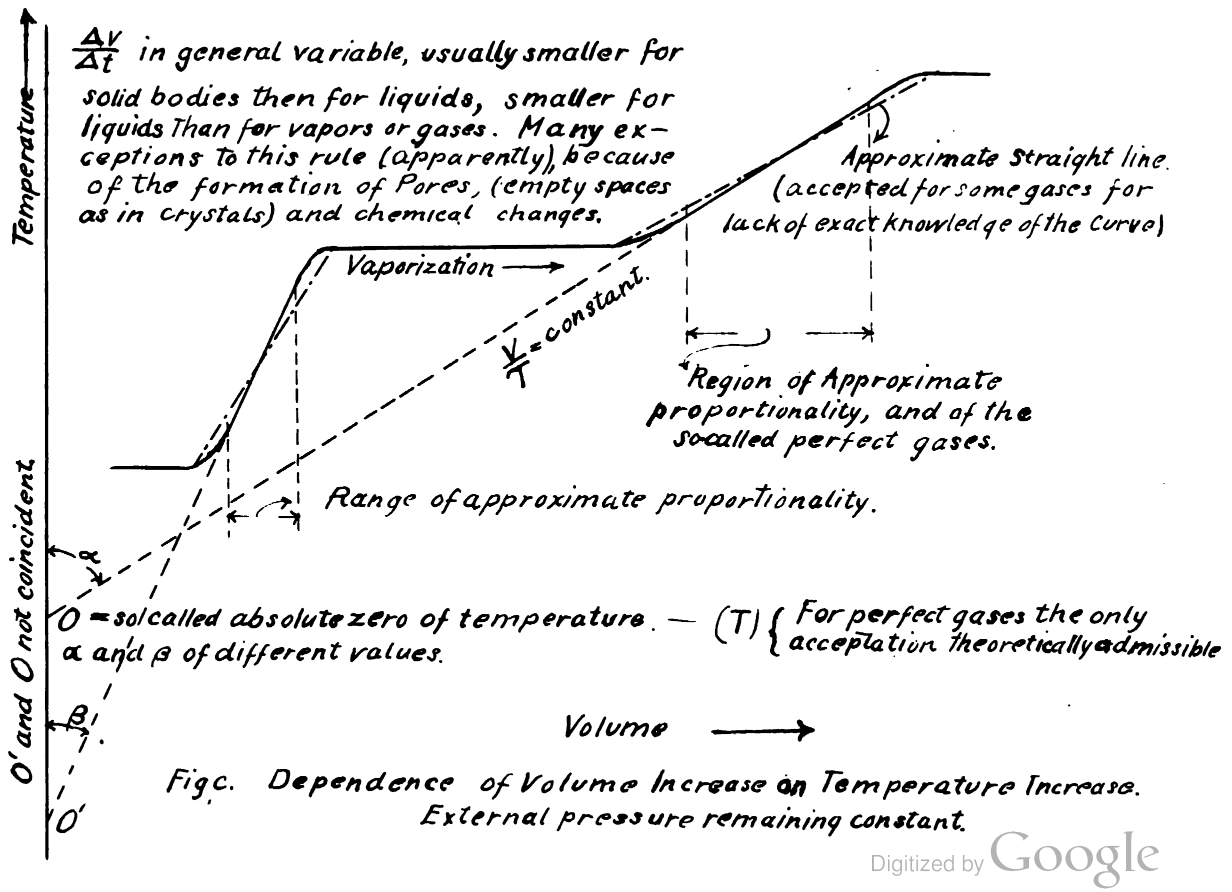

Temperature →
← Absolute bearing of the Abscissae
Perhaps at −∞ degrees Centigrade
Transition from (or into) unknown states (whose number may be infinite)
1–2 Heating (or cooling) of the solid.
2–3 Melting of Solid or Freezing of Liquid.
3–4 Heating (or cooling) of the Liquid.
4–5 Evaporation of Liquid or Condensation of Vapor
5–6 Heating (Superheating) or Cooling of the Vapor.
6–7 Transition into (or from) unknown higher (gaseous) States. (whose number may be infinite)
1
2
3
4
5
6
7
5. Point of dry saturated steam
Volume →

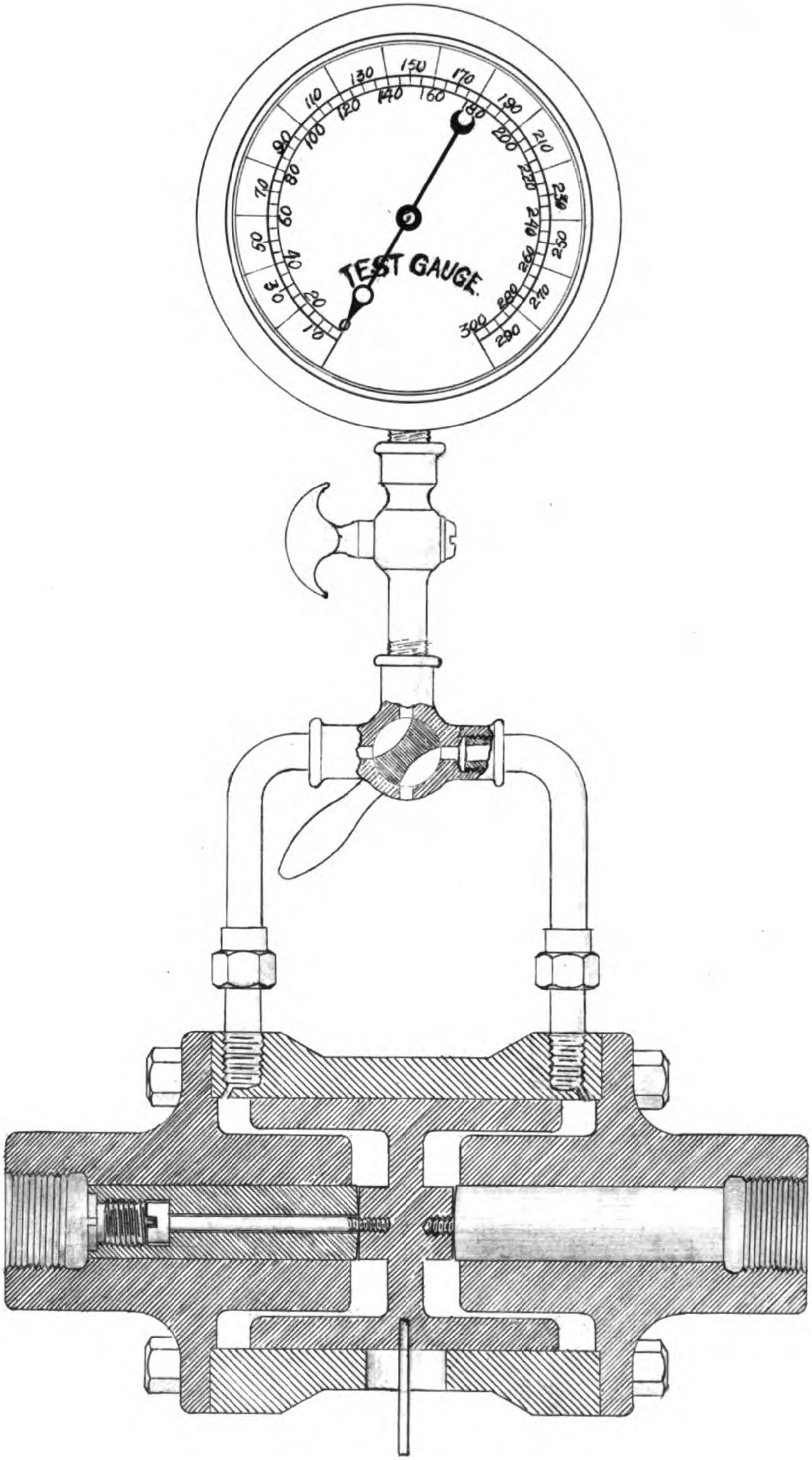
Fig. (a + b) – Conception of the Temperature-Volume Relations — External pressure constant.


Temperature →
O' and O not coincident
Vaporization →
$\frac{V}{T}$ = constant.
Approximate straight line. (accepted for some gases for lack of exact knowledge of the curve)
Region of Approximate proportionality, and of the so-called perfect gases.
Range of approximate proportionality.
α
β
O = so-called absolute zero of temperature. — (T) { For perfect gases the only acceptation theoretically admissible
α and β of different values.
O'
Volume →

$\frac{\Delta v}{\Delta t}$ in general variable, usually smaller for solid bodies then for liquids, smaller for liquids than for vapors or gases. Many exceptions to this rule (apparently), because of the formation of Pores, (empty spaces as in crystals) and chemical changes.

Fig. c. Dependence of Volume Increase on Temperature Increase. External pressure remaining constant.

PLATE X.



TEST GAUGE

APPROVED,

Storm Bull

June 1st. 1905.

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